PROPERTIES OF HYDRAZINE

I. QUANTITATIVE DETERMINATION OF HYDRAZINE

II. PREPARATION OF ANHYDROUS HYDRAZINE

III. PHASE EQUILIBRIA IN TERNARY SYSTEMS CONTAINING HYDRAZINE

BY

ROBERT ALLEN PENNEMAN

A. B., Millikin University, 1941
M. S., University of Illinois, 1942

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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PROPERTIES OF HYDRAZINE

INTRODUCTION

The interest in anhydrous hydrazine for possible use as a jet propulsion fuel prompted the author to undertake a study of methods for its preparation by the dehydration of hydrazine hydrate. An improved method, based on certain theoretical considerations, was proposed. An investigation of this method involved the assay of free hydrazine in concentrations up to 100%. During the investigation it was discovered that the system hydrazine-water-sodium hydroxide exhibits two liquid phases, within certain concentration and temperature ranges. This phenomenon was therefore subjected to quantitative study.

I. QUANTITATIVE DETERMINATION OF HYDRAZINE

A survey was made of recorded methods for the quantitative determination of hydrazine. Some of the available methods are:

1. *Direct acid titration[1]
2. **Combination acidimetric and oxidmetric method
3. *Direct iodate, using solvent[2]
4. *Direct iodate with internal indicator[3]
5. Indirect iodate[4]
6. *Direct iodine[2]
7. Indirect iodine[4]
8. *Direct permanganate[2]
9. *Indirect permanganate[2]

*Methods checked in the present study.
**A method proposed and evaluated by the author.

Excellent and reproducible results were obtained using methods 3, 4 or 6. Neither of the permanganate methods (8, 9) was found to be satisfactory. The direct acid titration

of free hydrazine with 0.5 *N* acid is satisfactory, using either methyl red or methyl orange as indicator and titrating to the color of a pH 4-4.5 buffer. If another base is present, the direct acid titration will not indicate the true amount of hydrazine. However, combination of the acidmetric with an oxidimetric method on one sample yields a procedure for determining both total base and hydrazine. Analyses of a synthetic mixture, prepared using a weight buret, appear in Table I.

TABLE *I*

Analyses of a Hydrazine and Ammonia Mixture by the Combination Acid-Iodate Method

% NH_3 Present	% NH_3 Observed	% N_2H_4 Present	% N_2H_4 Observed
2.87	2.92	44.22	44.22
2.87	2.87	44.22	44.26
2.87	2.92	44.22	44.21
2.87	2.88	44.22	44.26

Since solutions containing free hydrazine in appreciable concentration are subject to oxidation by atmospheric oxygen, fume badly, and absorb carbon dioxide, the following techniques are recommended:

1. Sample weighing should be made using weight burets or pipets.
2. The hydrazine should be added to water containing a slight excess of acid.
3. In the acidimetric titration of free hydrazine, recently boiled, oxygen and carbon dioxide-free water should be used for dilution of the sample.
4. For small samples, micro pipets should be used.

In the present study, involving analysis of free hydrazine of concentrations from 95-100%, micro pipets, 100-500 microliters in volume, were constructed from capillary tubing by

blowing two tiny reservoirs and drawing the capillary down at both ends. A 1 ml hypodermic syringe was used to fill the pipets. Since the capillary openings were extremely fine, the full pipets could be wiped and weighed with no additional precaution against hydrazine loss. Quantitative transfer of the sample was accomplished by discharging the full pipet into 50 ml of water and rinsing twice. The results in Table I were obtained using this sampling technique.

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II. PREPARATION OF ANHYDROUS HYDRAZINE

Introductory. The preparation of anhydrous hydrazine by the dehydration of hydrazine hydrate has been studied by various investigators. Three common materials which have been used as dehydrating agents are barium oxide[1,2], potassium hydroxide[3], and sodium hydroxide[4,1]. The dehydration processes have usually involved long reflux with the dehydrating agent followed by distillation in an inert atmosphere at reduced pressure. Some investigators have found it necessary to distil repeatedly and even to resort to fractional freezing to obtain 100% purity. In view of the fact that recorded data with respect to attainable purity are conflicting and previously recommended methods are time-consuming and inefficient, a further study of the dehydration of aqueous hydrazine was undertaken.

Theoretical. Sodium hydroxide forms a monohydrate of extremely low vapor pressure, (0.3 mm.) melting at 64.3°C[5],

while the hydration products of barium oxide and potassium hydroxide are solid up to the boiling point of hydrazine. It was decided to study the dehydration of hydrazine hydrate using sodium hydroxide since its successful use would offer two obvious advantages: a) its low cost relative to other dehydrating agents, and b) the ease of distillation from a completely liquid system. It was expected that the addition of sodium hydroxide in molar proportions to the water present in a hydrazine solution would allow the distillation of substantially anhydrous hydrazine from a system that is completely liquid above approximately 60°C. Fractionation of the vapor from such a composition would allow the preparation of anhydrous hydrazine.

Experimental. Anhydrous hydrazine was obtained in essentially quantitative yield by fractional distillation (at 80-100 mm.) from a hydrazine solution containing sodium hydroxide and water in equimolar quantities. The distillation was carried out above the melting point of sodium hydroxide monohydrate. At temperatures higher than approximately 60°C. the system is completely liquid. Within certain concentration ranges, this system consists of two liquid phases.

If no provision is made for fractionation of the vapor, i. e., simple distillation, approximately 80% of the hydrazine may be obtained as a product containing 97-99% N_2H_4. The remaining 20% of the hydrazine originally present distils as a fraction containing approximately 90% N_2H_4.

Technical caustic soda was substituted successfully for fused, or reagent sodium hydroxide, allowance being made for the water content of the commercial material.

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III. PHASE EQUILIBRIA IN TERNARY SYSTEMS CONTAINING HYDRAZINE

Introductory. During the course of experimental work on the preparation of anhydrous hydrazine as described in Part II, it was discovered that the reaction mixture separates into two liquid phases. The possibility of preparing hydrazine of high concentration by causing separation of a hydrazine-rich phase made desirable a quantitative study of this phenomenon.

Experimental. The system hydrazine - water - sodium hydroxide was studied quantitatively at 50, 60, 70, 90 and 100° to determine the area of limited miscibility and phase relationships which characterize varying mixtures of the three components. At temperatures from approximately 60°C. to the boiling point, this ternary system exhibits two liquid phases, within certain concentration ranges. At 50°C., a simple solubility curve is observed, with $NaOH \cdot H_2O$ in equilibrium with a saturated solution containing hydrazine, water, and sodium hydroxide.

Data summarized in Table II indicate that there is little change in the limiting composition of the conjugate liquid phases, or of the plait point, between 70 and 100°C. At 60°C., however, the area of limited miscibility is considerably smaller. Furthermore, the crystalline phase, $NaOH \cdot H_2O$ is obtained under certain conditions at this temperature, whereas at higher temperatures, anhydrous sodium hydroxide appears as the stable solid phase.

TABLE *II*

Summary of Plait Points and Limiting Compositions of Conjugate Liquid Phases

Temp., °C.	Material	% N_2H_4	% NaOH	% H_2O
100	upper phase	92.7	2.4	5.0
90	upper phase	92.2	2.0	6.0
70	upper phase	90.9	3.2	6.0
60	upper phase	77.5	9.3	13.0
100	lower phase	5.7	70.3	24.0
90	lower phase	5.9	69.3	25.0
70	lower phase	6.7	67.6	25.5
60	lower phase	19.0	51.4	29.5
100	plait point	45.9	27.9	26.0
90	plait point	45.6	28.2	26.0
70	plait point	45.4	28.5	26.0
60	plait point	45.5	29.6	25.0

An attempt was made to use other compounds forming stable hydrates to cause separation of hydrazine hydrate into two liquid phases. Negative results were obtained using potassium hydroxide, potassium carbonate, and sodium sulfate over the temperature range 25-100°C.

VITA

The author was born on February 5, 1919, in Springfield, Illinois, and attended the public schools of that city until his graduation from Feitshans High School in February, 1937. In the fall of that year he entered the James Millikin University at Decatur, Illinois, having been awarded a scholarship. During his senior year at Millikin he served as an assistant in chemistry. Upon graduation in 1941 with the degree of Bachelor of Arts, he shared first honors and received his degree Summa Cum Laude.

He entered the graduate school of the University of Illinois in September, 1941, on a graduate fellowship, and received the degree of Master of Science in chemistry in 1942. Between 1942 and 1946 he served as a research chemist on the Plutonium Project.

In 1946 he was awarded a National Research Council Fellowship, making it possible for him to complete his doctorate training. He is a member of the following societies: the American Chemical Society, Sigma Xi, Phi Lambda Upsilon, Alpha Chi Sigma, and the Kappa Society (Millikin).